PATENT SPECIFICATION

809,722

No. 13019/57.

Date of Application and filing Complete Specification: April 24, 1957.

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Index at acceptance:—Class 2(6), P2A, P2C(8C:10B:20A). P2(D1A:FX:K8:T2A).
International Classification:—C08d.

COMPLETE SPECIFICATION

Improvements in or relating to Nitrile Rubber Compositions and to Accessories manufactured therefrom for Electric Cables

We, PIRELLI SOCIETA PER AZIONI, a Company incorporated under the laws of Italy, of Viale Abruzzi 94, Milan, Italy, do hereby declare the invention, for which we pray that a Patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention relates to nitrile rubber compositions and to accessories manufactured therefrom for gas-pressure or oil-filled electric cables insulated with paper impregnated with mineral oils or with viscous or non-draining compounds having a basis of which have practically no detrimental effect on the dielectric characteristics of the insulating oils, that is on the dielectric losses and on the values of the specific electrical insulation of such oils.

Technological difficulties are encountered when it is required that the vulcanizable nitrile rubber composition should be easily mouldable or extrudable and that the vulcanizates should have a limited hardness. In fact it is well known that nitrile rubbers have a high nerve or snap which hinders, and in some cases absolutely prevents, obtaining moulded or extruded products having regular limited hardness. However, great importance is attached to this class of elastomers, both on account of the greater thermal stability of the vulcanizates in an environment devoid of oxygen (as generally happens in the practical use thereof), and because of their lesser tendency to contaminate the insulating oils.

At the present time it is possible to obtain, by suitable formulation, accessories having a nitrile rubber base which are resilient and [illegible] at 100°C, continually deteriorates until its dielectric power factor may teach a value of 0.2 and over, whilst the specific insulation value of the said oil, measured at 100°C. may fall to 1/100, 1/1000, and less, of its normal value.

It has also been ascertained that some plasticizers, of the ester type, such as tricresylphosphate and dioctylphthalate, when added directly to a mineral oil as used in cables, also increase its dielectric power factor

ERRATA

SPECIFICATION NO. 809,722

Page 1, line 82, *for* "teach" *read* "reach".

Page 2, line 30, *for* "insulation" *read* "insulating".

Page 3, line 46, *for* "Specification" *read* "Specific".

THE PATENT OFFICE,
3rd April, 1959

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This invention relates to nitrile rubber compositions and to accessories manufactured therefrom for gas-pressure or oil-filled electric cables insulated with paper impregnated with mineral oils or with viscous or non-draining compounds having a basis of mineral oils. In the manufacture of said cables it is frequently necessary to use gloves, tubes, packings and other accessories made of a sufficiently resilient material which withstands the swelling action of mineral oils and does not impair by contamination the good intrinsic dielectric properties of the oils with which the said accessories come into contact.

For this purpose there are commonly employed vulcanizates, which are obtained in various shapes by moulding or extrusion, based on polymerized chloroprene or nitrile rubber. In modern techniques there is an ever-increasing tendency to eliminate the use of polymerized chloroprene, because its vulcanizates contaminate the insulating oils with which they come into contact to a relatively high degree.

On the other hand, by using vulcanizates based on nitrile rubber it is very difficult to obtain products having good flexibility and limited hardness. However, great importance is attached to this class of elastomers, both on account of the greater thermal stability of the vulcanizates in an environment devoid of oxygen (as generally happens in the practical use thereof), and because of their lesser tendency to contaminate the insulating oils.

At the present time it is possible to obtain, by suitable formulation, accessories having a nitrile rubber base which are resilient and which have practically no detrimental effect on the dielectric characteristics of the insulating oils, that is on the dielectric losses and on the values of the specific electrical insulation of such oils.

Technological difficulties are encountered when it is required that the vulcanizable nitrile rubber composition should be easily mouldable or extrudable and that the vulcanizates should have a limited hardness. In fact it is well known that nitrile rubbers have a high nerve or snap which hinders, and in some cases absolutely prevents, obtaining moulded or extruded products having regular and perfect shapes. It is possible to neutralise the said elastomer nerve by means of suitable fillers, but this results in vulcanizates of a high degree of hardness (70-80 Shore). The simultaneous employment of suitable plasticizers and fillers enables perfect products to be obtained, namely extruded products with a smooth surface and having stable shapes and moulded products of complicated shapes, which are devoid of faults. However, all the usual plasticizers heretofore employed which are compatible with nitrile rubbers in the proportions adapted to produce a limited hardness in the vulcanizates are at least partially extracted by the cable insulating oils with which they come into contact causing a deterioration in the electrical properties of the oils. Thus for example an insulating oil, which normally shows a dielectric power factor (tan δ) of the order of 0.0005-0.0009 at 100°C., continually deteriorates until its dielectric power factor may reach a value of 0.2 and over, whilst the specific insulation value of the said oil, measured at 100°C. may fall to 1/100, 1/1000, and less, of its normal value.

It has also been ascertained that some plasticizers, of the ester type, such as tricresylphosphate and dioctylphthalate, when added directly to a mineral oil as used in cables, also increase its dielectric power factor

although to a smaller extent (from two to five times). Their behaviour is much worse when they are added to the composition constituting the vulcanizates which comes into contact with the insulating oil, probably owing to interaction with the ingredients which it is necessary to incorporate in the composition in order to obtain proper vulcanization.

The object of the present invention is to enable accessories for electric cables of the kind above mentioned to be made of nitrile rubber vulcanizates having suitable mechanical properties, for example hardness of the order of 40–70 Shore, tensile strength about 1 kg./sq.mm., elongation at break of the order of 400–500 per cent., permanent set of the order of 5 per cent. when tested in accordance with A.S.T.M. standards, and low thermoplasticity. Other objects of the invention are to provide vulcanizates with good technological properties, such as the easy processing of the uncured compound, which are suitable for the production of extruded articles having a smooth surface, which possess, according to requirements, good insulating or electrically conducting properties, and which above all are resistant to the swelling action of the insulation oils and do not affect the said oils by contamination.

For this purpsoe the vulcanizable composition according to the present invention comprises a solid butadiene-acrylonitrile copolymer of normal molecular weight, a liquid plasticizer consisting of a butadiene-acrylonitrile copolymer of low molecular weight defined by a viscosity ranging between 10,000 and 3,000,000 centipoises (cP) measured at 30°C., and additive materials comprising the usual vulcanizing and anti-oxidizing agents, a filler or fillers and an anti-adhesive agent, said additive materials being such as not to contaminate insulating oils with which the said composition may come into contact or cause undue deterioration in the dielectric properties of said oils. As examples of the solid butadiene-acrylonitrile copolymer of normal molecular weight there may be instanced the compounds known commercially under the various trade names "Hycar OR 15." "Hycar OR 25." "Paracril" and "Perbunan," and as an example of the liquid butadiene-acrylonitrile copolymer of low molecular weight there may be mentioned the compound known commercially under the trade name "Hycar 1312." The words "Hycar," "Paracril" and "Perbunan" just mentioned and also, in the case of "Hycar," referred to hereinafter in the specification, are Registered Trade Marks. The quantity by weight of the liquid butadiene-acrylonitrile copolymer of low molecular weight to that of the solid butadiene-acrylonitrile copolymer of normal molecular weight in the vulcanizable composition may vary from about 5 to 50 per cent., the former percentage giving a degree of hardness of about 70 Shore and the latter percentage giving a degree of hardness of about 40 Shore of the vulcanizate.

The solid butadiene-acrylonitrile elastomer of normal molecular weight serves to impart to the vulcanizate those mechanical properties which it would not be possible to obtain by the use only of the liquid elastomer of low molecular weight. On the other hand, the latter facilitates the processing of the uncured compound, even though it is suitable for obtaining vulcanizates of normal hardness (70–75 Shore).

With the mixture of the two elastomers there are also incorporated as above mentioned all the other ingredients which are necessary both for carrying out the vulcanization and for obtaining the mechanical properties which are desired and which are obtainable only by the addition of fillers. Thus, for example, the addition of a non-staining carbon black of the "Furnace," "Channel" or "Thermal" type in suitable proportions permits the obtaining of extruded articles having a smooth surface, such as tubes, gloves, packings and rods. Good vulcanizing agents are sulphur and tetramethylthiuram disulphide. Generally, the addition of zinc oxide or other activators is necessary in order to carry out a proper vulcanization, and the use of suitable anti-oxidants, such as phenyl beta-naphthylamine, is also advisable. For technological reasons it is also necessary to use a very small quantity of an anti-adhesive agent, such as stearic or palmitic acid, the anti-adhesive agent employed being a substance which prevents sticking of the uncured compound to the walls of the mould during the vulcanization and to the rolls of the mixer or other device during the mixing of the various ingredients for the preparation of the vulcanizable composition. Where stearic or palmitic acid is used the amount thereof is preferably of the order of about 0.1 to 0.2 per cent. by weight and should not exceed about 3 per cent. by weight of the total weight of the vulcanizable composition so as to ensure that the final vulcanizate obtained will not swell under the action of mineral oils with which it may come into contact or cause undue deterioration, by contamination, in the dielectric properties of the said oils.

One composition of a vulcanizable compound suitable for the extrusion and moulding of accessories of complex shape, having a Shore hardness of the order of 55–57, is given hereunder merely by way of example:—

Example of composition of the compound

	parts by weight
Solid Butadiene-acrylonitrile copolymer of normal molecular weight (Hycar OR 15 Easy Process) ..	480
Liquid Butadiene-acrylonitrile copolymer of low molecular weight (Hycar 1312)	130
Zinc oxide	50
Carbon black, "Fine Furnace" type	325
Stearic acid	1
Tetramethylthiuram disulphide ..	10
Sulphur	2
Phenyl beta-naphthylamine ..	2
Total ..	1000

The vulcanization conditions of the above compound were 30 minutes at 143°C.

5 grams of this compound in the form of a sheet 1 mm. thick, after vulcanization, were placed in contact for 48 hours with 95 grams of a good cable insulating oil at a temperature of 80°C. Subsequently the oil was removed from the vulcanized sheet and both the dielectric power factor (tan δ) and the specific electrical insulation value expressed in Megohm cm. were determined on it.

In the following Table there are given the characteristic values thus obtained (test A) in comparison with those determined on the same oil, after analogous thermal treatment, without placing it in contact with a vulcanized sheet of the said compound (blank test) and with those similarly obtained (test B) by the same treatment in the presence of an analogous vulcanized sheet of compound plasticized with a plasticizer of the ester type already known as being one of the less harmful electrically in connection with the effects of oil contamination.

	Dielectric power factor (tan δ)		*Specification insulation in Megohm cm.* 10^4	
	at 100°C.	*at* 80°C.	*at* 100°C.	*at* 80°C.
Blank test	0.0009	0.0006	7000	28000
Test A	0.0015	0.0001	1700	5000
Test B	0.027	0.016	84	130

The great advantage obtained by employing the vulcanizable composition according to the present invention for maintaining the optimum intrinsic electrical properties of the insulating oils employed in the manufacture of electric cables insulated with paper impregnated with mineral oils is therefore clearly apparent from the above Table.

WHAT WE CLAIM IS :—

1. A vulcanizable composition comprising a solid butadiene-acrylonitrile copolymer of normal molecular weight, a liquid plasticizer consisting of a butadiene-acrylonitrile copolymer of low molecular weight defined by a viscosity ranging between 10,000 and 3,000,000 centipoises (cP) measured at 30°C., and additive materials comprising the usual vulcanizing and anti-oxidizing agents, a filler or fillers and an anti-adhesive agent, said additive materials being such as not to contaminate insulating oils with which the said composition may come into contact or cause undue deterioration in the dielectric properties of said oils.

2. A vulcanizable composition according to Claim 1, in which the quantity by weight of the liquid butadiene-acrylonitrile copolymer of low molecular weight to that of the solid butadiene-acrylonitrile copolymer of normal molecular weight is about 5 to 50 per cent., the former percentage giving a degree of hardness of about 70 Shore and the latter percentage giving a degree of hardness of about 40 Shore of the vulcanizate.

3. A vulcanizable composition according to Claim 1 or 2, in which the vulcanizing agents employed are sulphur and tetramethylthiuram disulphide, and zinc oxide is used as the activator.

4. A vulcanizable composition according to Claim 1, 2 or 3, in which phenyl-beta-naphthylamine is employed as the anti-oxidant incorporated in the composition.

5. A vulcanizable composition according to Claim 1, 2, 3 or 4, in which the anti-adhesive agent incorporated in the composition is stearic acid in an amount not exceeding 3 per cent. by weight, and preferably of the order of about 0.1 to 0.2 per cent. by weight, of the total weight of the vulcanizable composition.

6. A vulcanizable composition according to Claim 1, 2, 3, 4 or 5, in which the filler incorporated in the composition consists of a non-staining carbon black of the "Furnace," "Channel" or "Thermal" type.

7. A vulcanizable composition substantially as described with reference to the Example hereinbefore mentioned.

8. Resilient accessory parts such as tubes, gloves, packings and rods, for oil-filled or gas-pressure electric cables, said parts being manufactured from a vulcanizable composition as claimed in any of the preceding claims.

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